

REPORT DOCUMENTATION PAGE			Form Approved OMB No. 0704-0188	
Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503.				
1. AGENCY USE ONLY (Leave blank)		2. REPORT DATE 05 January, 1998		3. REPORT TYPE AND DATES COVERED Technical 8/1/97 - 2/28/98
4. TITLE AND SUBTITLE Structural Distortion of Dendrimers on Gold Surfaces: A Tapping-Mode AFM Investigation			5. FUNDING NUMBERS N00014-93-11338 300x084yip 96PR0-1027	
6. AUTHOR(S) A. Hierlemann, J.K. Campbell, L.A. Baker, R.M. Crooks, A.I. Ricco				
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Department of Chemistry Texas A&M University College Station, Texas 77843-3255			19980109 081 30	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) Office of Naval Research 800 North Quincy Street Arlington, Virginia 22217-5000			10. SPONSORING/MONITORING AGENCY REPORT NUMBER	
11. SUPPLEMENTARY NOTES Prepared as a communication to the Editor in <i>J. Am. Chem. Soc.</i> , submitted 12/15/97				
12a. DISTRIBUTION/AVAILABILITY STATEMENT Reproduction in whole, or in part, is permitted for any purpose of the United States Government. This document has been approved for public release and sale; its distribution is unlimited.			12b. DISTRIBUTION CODE	
13. ABSTRACT (Maximum 200 words) Atomic force microscopy (AFM) investigations of polyamidoamine (PAMAM) Starburst™ dendrimers, generations 4 and 8 (G4, G8), absorbed on Au (111) surfaces were conducted. By controlling dendrimer concentration and exposure time during adsorption, coverages ranging from completely isolated molecules to a monolayer were prepared. The individual dendrimer molecules forming a monolayer were clearly imaged. Upon exposure to hexadecanethiol, the shapes of individual dendrimers change and they become taller and narrower as more stable thiol-Au bonds replace some of the amine-Au bonds. In the case of monolayers, exposure to hexadecanethiol causes the dendrimers to gradually agglomerate, forming dendrimer "pillars" up to 30 nm in height and freeing progressively more surface area for thiol adsorption. DTIC QUALITY INSPECTED 2				
14. SUBJECT TERMS			15. NUMBER OF PAGES 14	
			16. PRICE CODE	
17. SECURITY CLASSIFICATION OF REPORT Unclassified	18. SECURITY CLASSIFICATION OF THIS PAGE Unclassified	19. SECURITY CLASSIFICATION OF ABSTRACT Unclassified	20. LIMITATION OF ABSTRACT	

Structural Distortion of Dendrimers on Gold Surfaces: A Tapping-Mode AFM Investigation

Andreas Hierlemann,^{1,2} Joseph K. Campbell,¹ Lane A. Baker,¹ Richard M. Crooks^{1*} and Antonio J. Ricco^{2*}

¹ Department of Chemistry, Texas A & M University, College Station, TX 77843-3255,

Fax: (409) 845 1399, e-mail: crooks@chemvx.tamu.edu

² Microsensor R & D Department, Sandia National Laboratories, Albuquerque, NM 87185-1425,

Fax: (505) 844 1198, e-mail: ajricco@sandia.gov

* authors to whom correspondence should be addressed

We report an atomic force microscopy (AFM) investigation of generation 4 and 8 (G4, G8) polyamidoamine (PAMAM) Starburst™ dendrimers absorbed on Au (111) surfaces. Heights measured for isolated, adsorbed dendrimers are substantially lower than expected based on their bulk-phase dimensions indicating a severe surface-induced distortion. By controlling dendrimer concentration and exposure time during adsorption, coverages ranging from isolated molecules to a monolayer were prepared. Exposure of sub-monolayer-coverage dendrimer films to hexadecanethiol caused the shapes of the individual dendrimers to become taller and narrower as more stable thiol-Au bonds replace some of the amine-Au bonds originally holding the dendrimer in a "squished-on-the-surface" conformation. In the case of monolayers, exposure to

hexadecanethiol caused the dendrimers to gradually agglomerate, forming dendrimer "pillars" up to 30 nm in height and freeing progressively more surface area for thiol adsorption.

There is a vast literature relating to dendrimers,¹ but only few reports of imaging individual dendrimers using TEM,² STM,³ and AFM,^{4,5} or showing the grainy structure of a dendrimer monolayer using AFM.⁶ For our study, dendrimers⁷ were absorbed onto atomically flat Au (111) facets by dipping the Au substrate⁸ for 45 s (short soaking times were applied in order to get high resolution images of the dendrimers, which in our experience could not be achieved using long soaking times) in either a 10^{-7} M ethanolic solution (to form a monolayer), or a 10^{-9} M solution (for isolated molecules). Au substrates were then alternately rinsed with ethanol and water several times. To alter the shape of isolated dendrimers, samples were soaked for 4 h in a 1 mM ethanolic solution of hexadecanethiol (Fluka Chemicals, Buchs, Switzerland), then rinsed as described above. To induce agglomeration of dendrimers arranged in a monolayer, soaking time in hexadecanethiol solution varied from 24 to 110 h. All measurements were made at a minimum of five different sites on each of two identically prepared Au substrates, with consistent results. Tapping-mode AFM measurements (topographical data only) in air were performed using a Nanoscope III (Digital Instruments, Santa Barbara, CA) with an E-type scanner.⁹

We simultaneously investigated two different sizes of dendrimers: the soft and deformable G4 (ideal sphere diameter: 4.5 nm¹¹), and the larger G8 having a harder exterior (ideal sphere diameter: 9.7 nm¹¹). The results for G8 are displayed in Figure 1a - c. Figure 1a shows the topography of the Au surface covered with isolated G8 dendrimers. In the upper right corner, an Au step edge is visible; the height of such edges (0.24 nm) provides an accurate vertical scale reference. The measured diameter of the adsorbed G8 dendrimer is approximately 20 nm, but as discussed below, the lateral dimensions are convoluted with the AFM tip shape. Nevertheless, the

height data in Figure 1b are reliable. Within experimental error (0.1 - 0.2 nm), the height of the G8 dendrimers on a bare Au surface ranges between 3.5 and 4.0 nm. The variation in heights and lateral size may arise from a distribution of molecular sizes resulting from the synthesis,^{2b} slight tip-induced deformation by the tapping process,^{6,10-13} and differences in the adsorption geometry. The measured height is about 60% less than the ideal sphere diameter of 9.7 nm.⁹ Tsukruk *et al.* reported the thickness of G6 monolayers adsorbed on Si as 2.8 nm and of G10 monolayers as 5.6 nm.⁶ Those heights are comparable to our results for G8 on Au. A possible explanation for the major discrepancy between measured and ideal-sphere diameters is the "pinning down" of the dendrimers to the surface via a number of fairly strong substrate-amine bonds.¹⁴ This is in contrast to the weak mica- or graphite-carbosiloxane dendrimer interactions,⁴ for which deviations from ideal-sphere diameter are reported to be minor. This "pinning down" is definitely more pronounced in the case of isolated dendrimers on a metal surface than for monolayers, where intermolecular interactions between the spheres affect their conformation.

Figure 1c shows the profile of adsorbed G8 dendrimers after soaking for 4 h in hexadecanethiol. Their surface density generally diminishes, some dendrimers having been replaced completely by the alkanethiols since the amine-Au interactions are challenged by thermodynamically more stable thiol-Au bonds. The height of the dendrimers remaining on the surface increases reproducibly from 3.5 - 4.0 to 5.0 - 6.5 nm. The noise on the baseline (0-nm level) also increases due to the presence of the thiol layer. The length of the hexadecanethiol chains is approximately 2 nm, and our 5.0 - 6.5 nm height range was measured from the terminal methyl groups; thus, the height of the dendrimers would be 7.0 - 8.5 nm after correcting for the thickness of the hexadecanethiol layer. While it is difficult to estimate how much the thiols are deformed by the tapping tip, interfacial force microscopy measurements indicate that the frequency

and/or vertical velocity of the vibrating tip are probably too high to cause kinks in the alkane chains.¹⁵ With or without correction for the added thickness of the alkanethiol layer, the 1.5 or 3.5 nm increase in dendrimer height is significant.

Thiol adsorption also compresses the dendrimers laterally, changing them from an oblate to a prolate shape as they lose more and more amine-Au links. In addition, some dendrimers can now be moved even by a slightly tapping tip (dragging traces) as has been previously observed on low-energy surfaces.⁴ The compressed state is stable for some time: even after 24 h in the hexadecanethiol solution, the height of the remaining isolated dendrimers changes no further compared to their shape after the initial 4 h treatment. However, extended exposure to a hexadecanethiol solution ultimately leads to displacement of the dendrimers from the surface altogether.¹⁶

Figures 1d - e show the corresponding data for G4 dendrimers. The dark area in the upper left corner of Figure 1d is an Au step edge. The measured height of the G4 dendrimers on a bare Au surface is 0.5 - 0.8 nm (1.8 nm for a G4 monolayer in ref. 6). Again, the lateral dimension (ca. 15 nm) is convoluted with the tip shape. By exposing the Au substrate to hexadecanethiol, the height of the G4 dendrimers increases to 1.5 - 2.0 nm above the thiol level, or about 2.0 - 2.5 nm in overall height.

Figure 2 shows a freshly prepared monolayer of G8 dendrimers. It is apparent that the monolayer is composed of aggregates of discernible individual dendrimers (black areas are the bare Au surface). In contrast to Figure 1, it is striking that there are no isolated dendrimers anywhere on the surface, only aggregates or, at the very least, strings composed of several interconnected dendrimers. Apparently, intermolecular interactions between dendrimers are strong enough to compensate for some lost dendrimer-Au interactions. Whether these

intermolecular interactions are hydrogen bonds of the terminal groups at the outer dendrimer surface, or a kind of interdigitation (which has been found not to be present in solution¹⁷), cannot be determined from our data.

In comparing the size of the G8 dendrimers in Figures 1 and 2, the lateral dimensions of isolated dendrimers appear much larger than in the monolayer. This is a consequence of the convolution of the tip shape with that of the dendrimer.¹⁸ In the present case, simple considerations suffice to estimate the magnitude of this effect. We assume a spherical tip shape. Because their height is 3.5 - 6.5 nm, the G8-dendrimers are contacted only by the apex of the tip (apex radius is 5 - 10 nm¹⁹). In rough approximation, therefore, the spherical tip rides over deformed spheres (dendrimers) of comparable size, resulting in the addition of about twice the tip radius to the actual size of the isolated dendrimers. This consideration does not hold for the smaller G4 dendrimers, for which much less than twice the tip radius is added to the lateral dimensions.^{4,20} In the case of monolayers, the tip does not reach the Au surface, riding instead on the tops of the dendrimer spheres, the result being negligible addition to the lateral dimensions.

In Figure 3, the results of exposing a monolayer of G8 to hexadecanethiol are presented. Figure 3a shows a G8 monolayer similar to that shown in Figure 2; the surface has a grainy structure, 3 - 4 nm in height. After a 24-h exposure to hexadecanethiol, the picture changes completely: the dendrimers vacate the surface in favor of the thiols, piling up to form aggregates reaching heights of 8 - 10 nm, and individual dendrimers are no longer recognizable.¹⁶ This aggregation, as opposed to loss of the dendrimers into solution, demonstrates the relatively strong intermolecular forces between dendrimers. After 48 and 110 h (Figures 3c, 3d), progressively more of the surface is covered by the thiols and the height of the aggregates increases further: ca. 15 - 18 nm at 48 h; ca. 25 - 30 nm at 110 h. Concurrently, the surface area covered by the

dendrimers decreases drastically. After 110 h, it is possible to image the Au step edges again in the areas now covered by the thiol. Ultimately, the surface will be fully thiol-covered, and completely devoid of dendrimers.¹⁶

In summary, at submonolayer coverage, the dendrimer shape changes from spherical to oblate upon adsorption to Au. Subsequent coadsorption of alkanethiols results in a lateral compression of the dendrimers and a substantial height increase, but the surface mobility of the isolated dendrimers is insufficient for them to agglomerate. In contrast, dendrimer monolayers are composed of agglomerates or strings of discernible individual dendrimers. Upon exposure to hexadecanethiol, dendrimer-dendrimer contacts provide an energetically favorable pathway for the dendrimers to phase segregate into pillars, while progressively more of the surface is covered by thiols.

Acknowledgments

A.H., J.K.C., L.A.B., R.M.C. gratefully acknowledge the National Science Foundation (CHE-9313441), the Robert A. Welch Foundation, Sandia National Laboratories, and the Office of Naval Research for support of this work. We thank Mr. Mark Kaiser of Dendritech Inc. (Midland, MI) for providing samples of the Starburst™ dendrimers. Helpful discussions with Prof. Scott Perry (University of Houston) are also acknowledged. Work at Sandia was supported by the United States Department of Energy under Contract DE-AC04-94AL85000. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed-Martin Company, for the United States Department of Energy.

Abstract

Atomic force microscopy (AFM) investigations of polyamidoamine (PAMAM) Starburst™ dendrimers, generations 4 and 8 (G4, G8), absorbed on Au (111) surfaces were conducted. By controlling dendrimer concentration and exposure time during adsorption, coverages ranging from completely isolated molecules to a monolayer were prepared. The individual dendrimer molecules forming a monolayer were clearly imaged. Upon exposure to hexadecanethiol, the shapes of individual dendrimers change and they become taller and narrower as more stable thiol-Au bonds replace some of the amine-Au bonds. In the case of monolayers, exposure to hexadecanethiol causes the dendrimers to gradually agglomerate, forming dendrimer "pillars" up to 30 nm in height and freeing progressively more surface area for thiol adsorption.

References

1. a. Newkome, G.R.; Moorefield, C.N.; Voegtle, F. *Dendritic Molecules: Concepts, Synthesis, Perspectives*, VCH, Weinheim, 1996.
- b. Newkome, G.R. *Advances in Dendritic Macromolecules*, JAI press, Greenwich, Connecticut, Vol.1, 1994, Vol.2, 1995.
- c. Fréchet, J.M. *Science*, 1994, *263*, 1710.
- d. Tomalia, D.A.; Durst, H.D. in *Topics in Current Chemistry*, Vol. 165, Weber, E., Ed.; Springer Verlag, Berlin, 1993, p.193.
- e. Zeng, F.; Zimmerman, S.C.; *Chem. Rev.* 1997, *97*, 1681-1712.
2. a. Tomalia, D.A.; Baker, H.; Dewald, J.; Hall, M.; Kallos, G.; Martin, S.; Roeck, J.; Ryder, J.; Smith, P. *Macromolecules* 1986, *19*, 2468.
- b. Jackson, D.L.; Chanzy, H.D.; Booy, F.P.; Tomalia, D.A.; Amis, E.J. *Proceedings ACS-Meeting* 1997, Las Vegas, Vol. 77, *Polymeric Materials, Science and Engineering*, 222-223.
3. Nevemov, I.; Kurnikov, I.; Nicolini, C. *Ultramicroscopy* 1995, *58*, 269-274.
4. Sheiko, S.S.; Eckert, G.; Ignateva, G.; Muzafarov, A.M.; Spickermann, J.; Raeder, H.J.; Moeller, M. *Macromol. Rapid Commun.* 1996, *17*, 283-297.
5. Takada, K.; Diaz, D.J.; Abruña, H.D.; Cuadrado, I.; Casado, C.; Alonso, B.; Moran, M.; Losada, J. *J. Am. Chem. Soc.* 1997, *119*, 10763-10773.
6. Tsukruk, V.V.; Rinderspacher, F.; Bliznyuk, V.N. *Langmuir* 1997, *13*, 2171-2176.
7. Starburst™ PAMAM dendrimers were generously donated by Dendritech Inc. Midland, MI.
8. Au substrates were prepared by melting and flame annealing wires to form Au balls with single-crystalline (111) facets.

9. Tapping-mode cantilevers (Digital Instruments, Santa Barbara, CA) had resonance frequencies of 260-280 kHz, force constants of 20-100 N/m, and tip apex radii from 5 to 10 nm. The cantilevers were operated at an A_0 of 4 V (40 - 60 nm) and a ratio of A_{sp}/A_0 of 0.8, corresponding to "slight tapping" (see ref. 10). The scan rate for images of all sizes was 2 Hz. Images included 512 x 512 data points and were flattened after recording using algorithms contained in the software; a low-pass filter was applied once.

10. Bar, G.; Thomann, Y.; Brandsch, R.; Cantow, H.-J.; Whangbo, M.-H. *Langmuir* 1997, **13**, 3807.

11. Technical data provided by Dendritech Inc., Midland, MI.

12. Whangbo, M.-H.; Magonov, S. N.; Bengel, H. *Probe Microscopy* 1997, **1**, 23-42.

13. Tsukruk, V.V.; Reneker, D. H. *Polymer* 1995, **36**, 1791.

14. a. Tokuhisa, H.; Zhao, M.; Baker, L. A.; Phan, V. T.; Dermody, D. L.; Garcia, M. E.; Peez, R. F.; Mayer, T. A.; Crooks, R. M. manuscript in preparation.

b. Wells, M.; Crooks, R. M. *J. Am. Chem. Soc.* 1996, **118**, 3988.

15. Lackowski, W. H. personal communication.

16. Loss or aggregation of dendrimers has been found to occur at short adsorption times (here 45 s.) of the dendrimers. Longer deposition times lead to more stable layers and less reversible dendrimer adsorption, see ref. 14a.

17. Uppuluri, S.; Tomalia, D. A.; Dvornic, P. R. Proceedings ACS-Meeting 1997, Las Vegas, Vol. 77, Polymeric Materials, Science and Engineering, 222-223.

18. a. Keller, D. *Surf. Sci.* 1991, **253**, 353-364.

b. Keller, D.; Franke, F. S. *Surf. Sci.* 1993, **294**, 409-419.

19. Technical data provided by Digital Instruments, Santa Barbara, CA.

20. Garcia, V. J.; Martinez, L.; Briceño-Valero, J. M.; Schilling, C. H.; *Probe Microscopy* 1997, 1, 107-116.

Figure Captions

Figure 1.

Topographic images of G8 (a) and G4 (d) dendrimers distributed on a Au (111) surface. Profiles (side views of images as shown in (a)) of G8 and G4 dendrimers on the bare Au surface (b, e), and after exposure to hexadecanethiol for 4 h (c, f, same surface, but different region). A major consequence of thiol adsorption is to decrease the area covered by dendrimers while increasing their height.

Figure 2.

Topographic image of a G8 monolayer on Au (111); individual G8 dendrimers are discernible.

Figure 3.

Height plots of a G8 monolayer on bare Au (a), and after a range of soaking times in ethanolic hexadecanethiol (1 mM) solutions: 24 h (b), 48 h (c), and 110 h (d). As the thiol occupies progressively more of the surface, the dendrimers aggregate into progressively higher pillars.

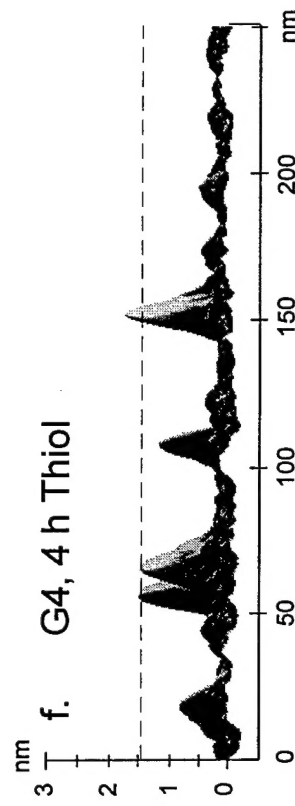
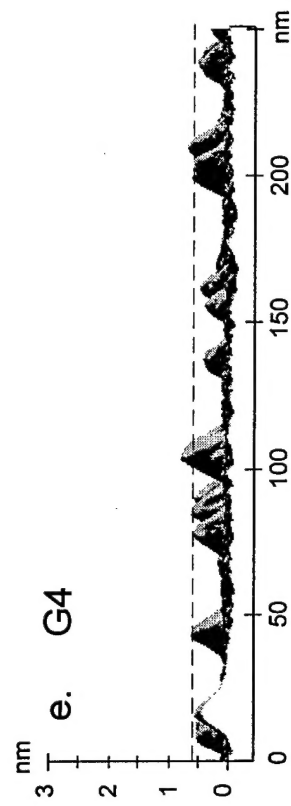
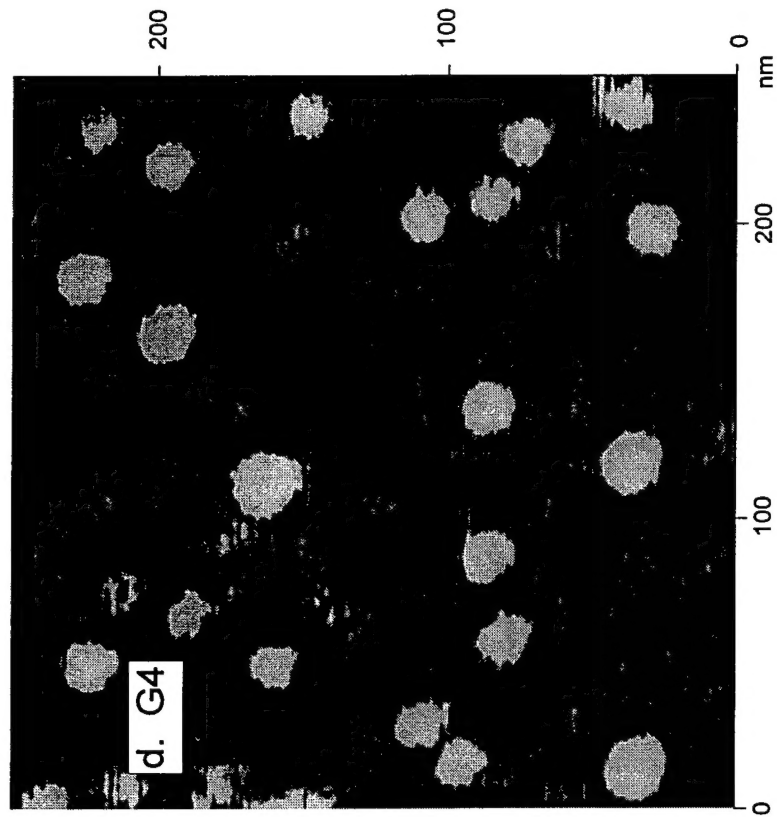
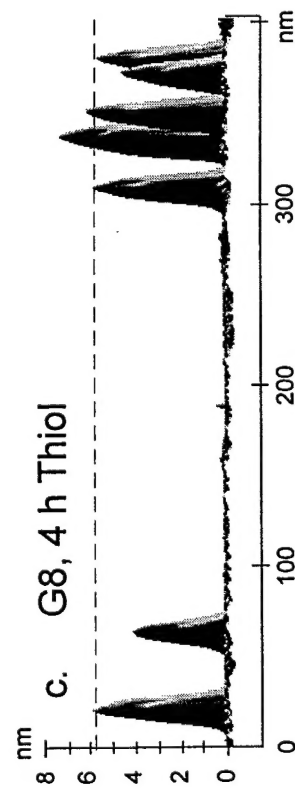
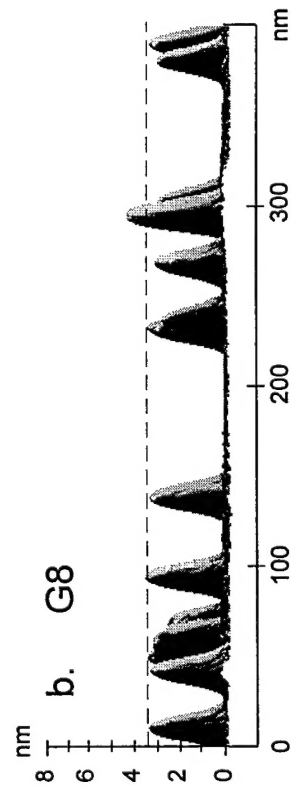
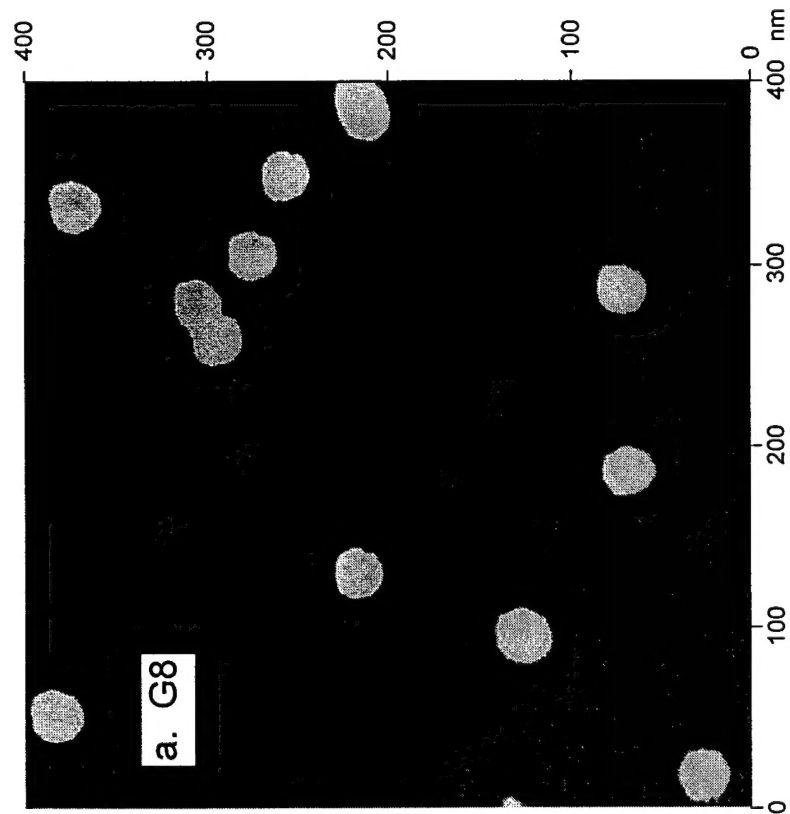


Fig. 1 Hierlemann et al.

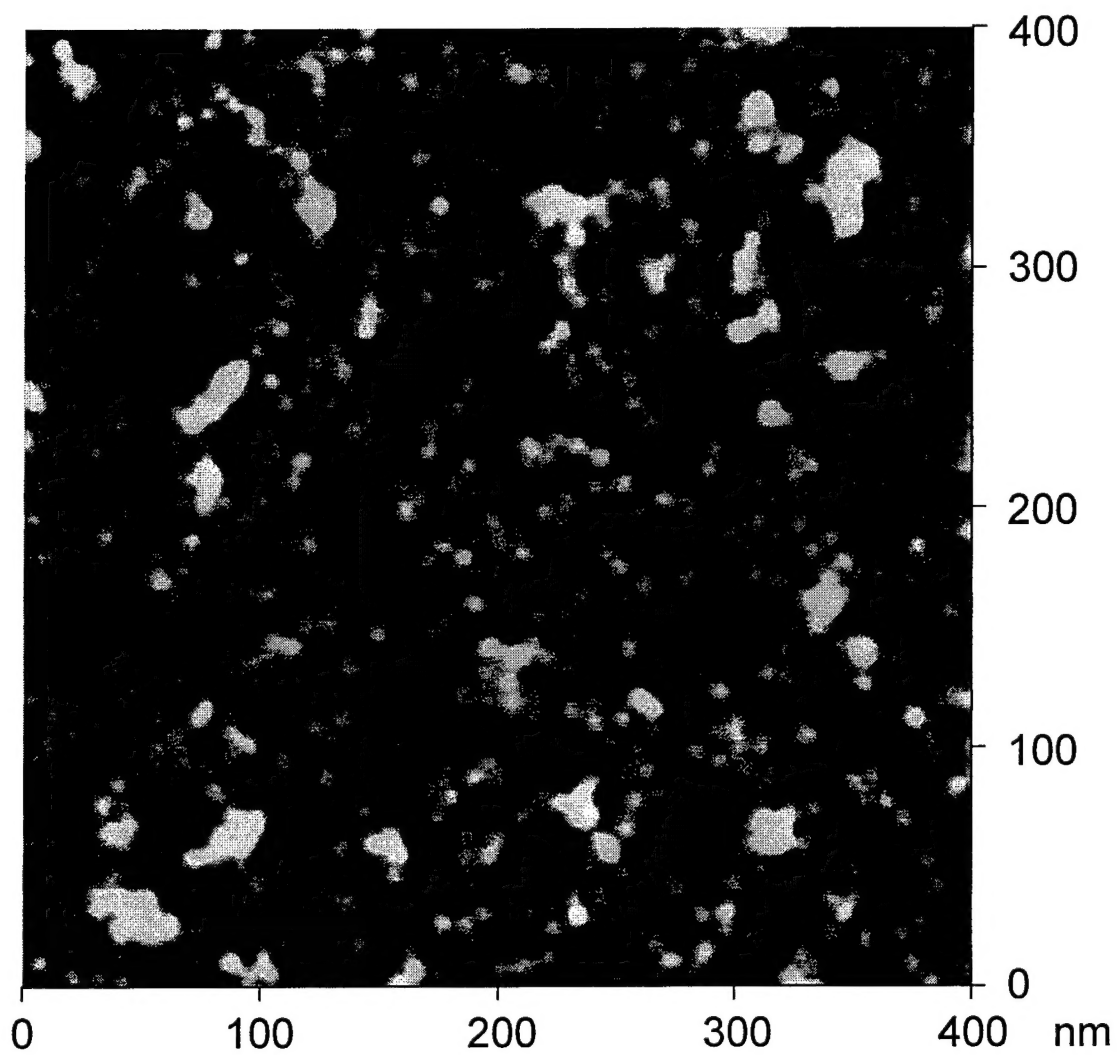


Fig. 2 Hierlemann et al.

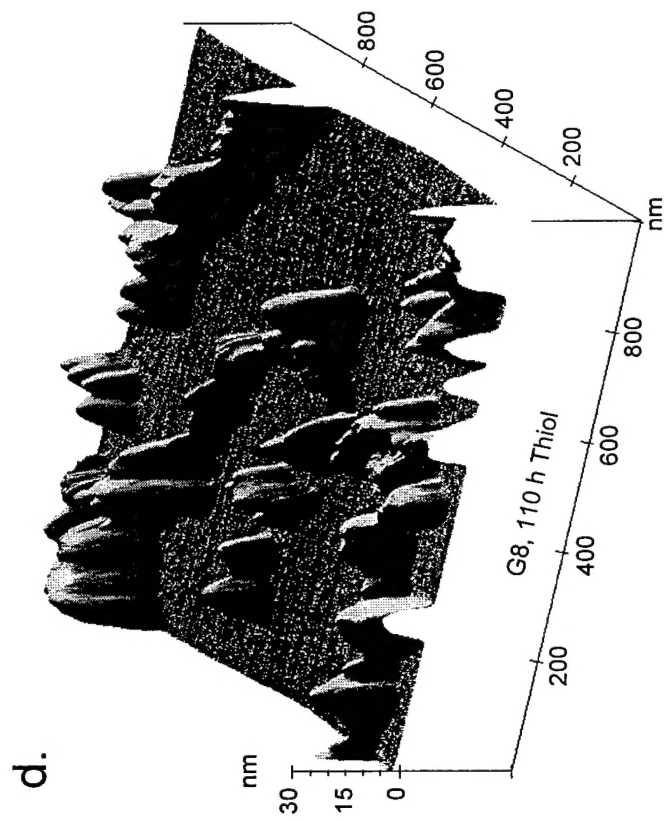
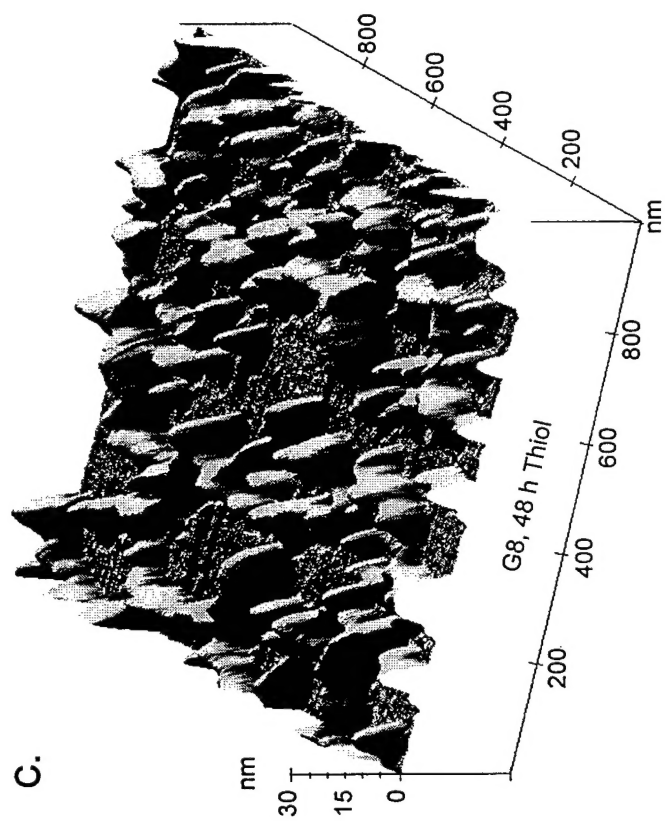
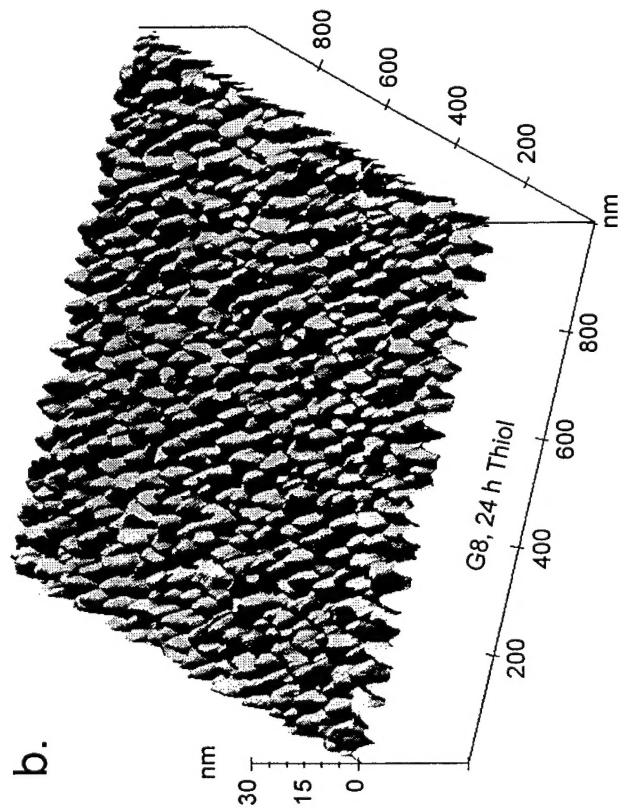
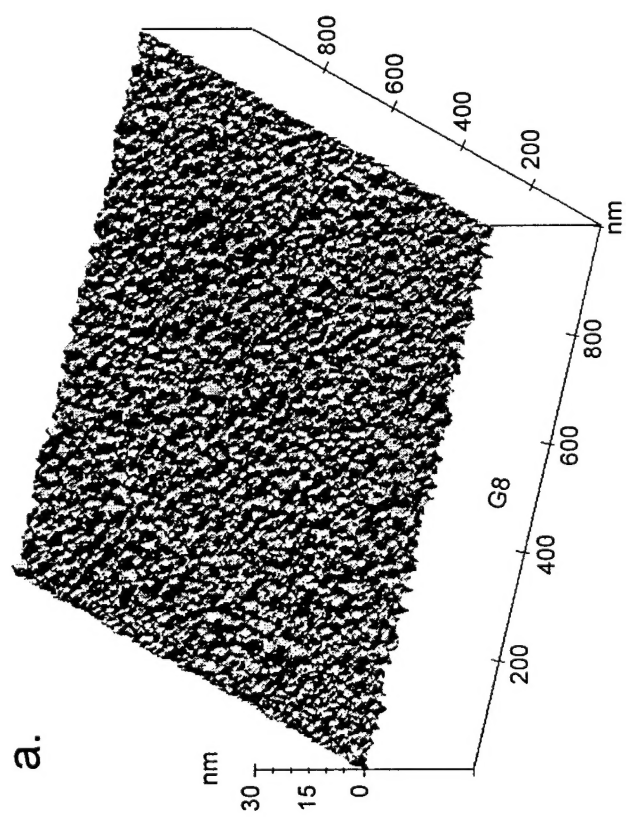


Fig. 3 Hierlemann et al.